

COMBUSTIVE DEMILITARIZATION OF EXPLOSIVES, TOXIC COLORED SMOKES, CHEMICAL AGENTS AND RELATED MUNITIONS BY A MILITARY INCINERATOR; DESTRUCTION OF FILLERS BY HYDROTHERMAL OXIDATION

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ABSTRACT

Most coloring agents used in older markers, signals and smoke munitions are carcinogenic or suspected carcinogens, but are still abundant in the military inventory. Confirmation of acceptable alternatives and development of safe disposal methods are thus important. Formulations for new items are chosen to minimize risks. Two successful methods are reported here for combustive destruction of colored smokes and many other military items. See the project reports^{1,2} for additional details and a literature summary on hydrothermal methods used for treatment of propellants, explosives and pyrotechnics (PEP).

Reaction temperature, feed rates, and etc., have been established for successful destruction of signal devices and bulk colored filler mixes, by incineration in the APE-1236M1 military kiln. This method has been successful also for bulk explosives and several types of munitions.

High pressure hydrothermal oxidation in the supercritical range also gave over 99% destruction and removal efficiency (DRE) for bulk colored smoke mixes, red-water, common explosives and a nerve agent simulant containing the toxic organic phosphate moiety.

MILITARY INCINERATORS

APE-1236M1 ROTARY KILN

The Ammunition Peculiar Equipment (APE) Model 1236 rotary kiln designed by AED has been a work-horse incinerator for decades for deactivation of bulk PEP, small arms, grenades, rocket motors and other munitions which could be cut into pieces shorter than about 8 or 10 inches to pass through the feed chute. PEP feed rate is usually about 200-300 lbs/hour, 400 for some items. The M1 version of the APE-1236 is a modern upgrade^{3,4a} which conforms to environmental regulations, particularly for Part B permits under the Resource Conservation and Recovery Act (RCRA) at several military installations. It has state-of-the-art baghouse, afterburner, modern control circuitry, fugitive emission control, and an automatic feed system that holds to the permitted feed rate for any munition being treated. The AED experimental APE-1236M1 was used for smoke munitions and some PEP runs reported here.

Approved for public release; distribution unlimited. Presented at the 27th DOD Explosives Safety Seminar, 20-22 August 1996, Sahara Hotel, Las Vegas, Nevada.

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE AUG 1996		2. REPORT TYPE		3. DATES COVERED 00-00-1996 to 00-00-1996	
4. TITLE AND SUBTITLE Combustive Demilitarization of Explosives, Toxic Colored Smokes, Chemical Agents and Related Munitions by a Military Incinerator; Destruction of Fillers by Hydrothermal Oxidation			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Tooele Army Depot,SIOTE-AE,Tooele,UT,84074-5004			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM000767. Proceedings of the Twenty-Seventh DoD Explosives Safety Seminar Held in Las Vegas, NV on 22-26 August 1996.					
14. ABSTRACT see report					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Some items were treated at newly upgraded APE-1236M1 units at other locations. Operating ranges were generally 1000 to 1400 °F for the primary firing chamber temperature, 1400 to 1600 °F for the afterburner temperature, 5 to 15 minutes residence time for feed-stock solids.

CONTAMINATED WASTE PROCESSOR (CWP), AND APE-2048 CHAMBER FURNACE

The CWP is an integrated furnace/pollution control complex (not an APE model), designed to deactivate waste that is contaminated with small amounts of explosive. The incinerator is a car-bottom chamber furnace fed from a large work room which has atmospheric control of fumes from incinerated baskets that can be cooling while fresh baskets are fired. It is a flashing furnace to burn off traces of PEP from metal equipment or munition parts for reuse, or for recovery of metals. It is a combustion furnace for paper, fabric, wood, plastic, etc., contaminated with PEP from munition operations. The CWP has a continuous feed option that can shred feed stock as large as a refrigerator. The furnace itself was developed by AED in the style of the old APE-2048 car-bottom chamber furnace. Now the APE-2048 is being upgraded to a new style of chamber furnace. This study did not test chamber furnaces, but they are well suited to incinerate waste contaminated with smoke mixtures.

OTHER MILITARY FURNACES

Some military installations use rotary kilns or chamber furnaces that differ from those described above, as there is no requirement to use standard military models.

DYES AND SMOKE MUNITIONS

Old-style dyes for military markers and grenades are polycyclic or aromatic amino, hydroxy, azo and keto compounds, in which unsaturation is conjugated with the aromatic structure. Such moieties are known to cause chromosome mutations which may lead to cancer. Coloring agents for new munitions are chosen to minimize potential carcinogenicity, which increases cost, but allows recycling of the dyes without high health risks. This project addresses the need to establish deactivation methods for coloring agents and smoke formulations. Two-hundred to six-hundred pounds each of several formulations of smoke mix were studied. Four colored smoke mixes were tested in bulk: green, yellow, red and violet formulations listed below, as fillers for markers and smoke devices. Others were tested in the form of finished signal or smoke grenades: the MK-124 Signal for use as a hand-held flare at night or an orange smoke generator by day, and MK-99-MOD-1 as a flare at night or a yellow smoke by day, the MK-7 black smoke generator -- intended to be dropped from an aircraft, the XM-82 grenade is a new smoke generator based on dispersion of TiO₂.

No smoke emissions were observed from the AED experimental APE-1236M1 furnace at following feed rates for bulk smoke mixes and munitions. The examples of bulk PEP listed are from successful Trial Burn Tests which passed for issuance of RCRA Part B permits at various APE-1236 locations,⁵ and from approved feed rates for the APE-1236 with a positive feed system.^{4b}

Dye formulations include colored organic structures usually mixed with various amounts of sodium carbonate, sulfur, dextrin, and potassium chlorate which combusts to potassium chloride salt rather than giving off chlorine. Note the high recovery of ionic K^+ and Cl^- from the furnace ash assay, Table 2. The yellow dye was changed in the 1980's from auramine, a bis-[dimethylaminophenyl]-methyline, to solvent yellow 33, which is 2-(2'-quinolyl)-1,3-indandione to reduce the toxicity risk. However, all the dye structures are of the types present in known carcinogens, and should be handled without bodily contact. The green mix contains some of the yellow dye along with a green dye, 1,4-di-p-toluidinoanthraquinone. The red dye is disperse red 9, which is 1-methylaminoanthraquinone. The violet mix contains some of the red dye along with a violet dye, 1,4-diamino-2,3-dihydroanthraquinone. The orange dye is solvent orange 7, which is 1-(2-metaxylene-azo)-2-naphthol. The black smoke mix contains anthracene and hexachloroethane, both of which generate black carbon powder when ignited with the magnesium powder present. The new white smoke grenade contains white powdered titanium dioxide which becomes dispersed by the energetics present.

Table 1. Non-Polluting APE-1236 Incineration Feed Rates for Smoke Mixtures, Smoke Munitions and PEP

Items/h	Lbs PEP/h	APE-1236 Feed-Stock Item
240	442	XM-82 Smoke grenade (480 lbs total/h)
120	31.7	MK-99-MOD-1 Signal (210 lbs total/h)
400	80	MK-124 Signal (1040 lbs total/h)
80	30.5	MK-7 Signal (163 lbs total/h)
300-400		Bulk smoke mix: green, yellow, red, or violet
350		TNT explosive ^{4b}
231		TNT/cobs 3:1 ^{5d}
200		RDX explosive ^{5a}
200		Comp-A3 explosive ^{4b}
201		Comp-A5 explosive ^{5a}
300		Comp-B explosive ^{4b}
271		H-6 explosive ^{5d}
400		Octol explosive ^{4b}
180		Black powder ^{4b}
162		Black powder 1:1 with lime ^{5c}
240		M1 propellant ^{4b,5c}
240		M1 propellant with trace metals ^{5e}
125		M7 propellant with trace metals ^{5e}
200		M9 propellant ^{4b}
203		M10 propellant ^{5a}
240		M30 propellant ^{5c}
200		PBX0280 propellant ^{5d}
40.5		HI-SKOR 700X propellant ^{5b}
182		IMR-5010 propellant ^{5b}

Table 2. Analyses for Smoke Munitions Treated in APE-1236M1*

	Cd TCLP	Pb TCLP	Tot Org CARBON	K ⁺	Cl ⁻	mg/m ³ TSP	Smoke Reading
Green mix untreated	ND 0.05	ND 0.05					
Green mix residue	ND 0.05	ND 0.05	31700	176200	160700		
Green mix cyclone				108050	124500		All 0.0
Green mix HI-temp cooler				73800	2670		All 0.0
Green mix/MK124 HI-temp	9.52	1.73					All 0.0
Green mix LO-temp cooler				5770	3740		All 0.0
Green mix baghouse				143600	95200		All 0.0
Green mix/MK124 baghouse	14.5	14.73					All 0.0
Green mix stack dry trap			ND				All 0.0
Green mix stack bubbler	ND 0.02	0.14	ND				All 0.0
Yellow/red/violet residue	ND 0.02	ND 0.05					
Yellow mix cyclone				70710	65500		All 0.0
Red/violet mixes cyclone				97130	115700		All 0.0
Red mix HI-temp cooler				72940	13140		All 0.0
Violet mix HI-temp cooler				52460	54500		All 0.0
Yellow/Violet LO-temp cooler	2.93	4.86					All 0.0
Yellow/Red/Violet baghouse	9.54	2.90					All 0.0
MK9 Signal Baghouse	1.2	10.0	120				All 0.0
XM82 Smoke grenade							
Ash residue	6.7	65.1					
Baghouse dust	60.9	8421					
Stack gas						<0.014	All 0.0
MK99MOD1 Smk/Illum Signal							
Ash residue	ND 0.05	ND 0.25					
Baghouse dust	ND 0.05	ND 0.25					
Stack gas							All 0.0
TCLP HW level	1.0	5.0					

ND = None detected at PPM level noted.

*TCLP HW = PPM values of Toxic Characteristic Leaching Procedure, Hazardous Waste values are underlined, TCLP values were not in the HW range for As, Ba, Cr, Hg, Se, Ag.

HIGH-PRESSURE HYDROTHERMAL OXIDATION

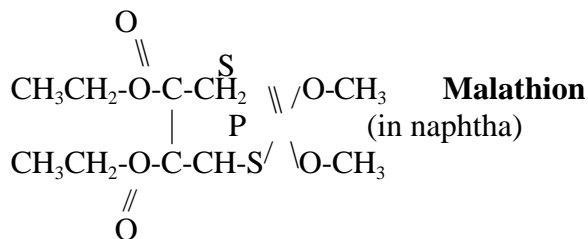
A small pilot plant was used for first stage proof that high %DRE can be attained with items of interest in this study. The furnace consisted of a 6.35 mm OD tube 6.1 m long mostly enclosed in a furnace. Most runs were made at 400 to 500 °C. Various alloys were used for the tube, with reaction volumes in the 16 to 23 cm³ range. Scale up is to be expected in two ways, first by enlargement of the diameter of the tubular flow to 1 or 2 inches, and thereafter by an increase in the number of tubes handled by the same furnace. The system used water as the carrier. Various devices were used to avoid plugging from inorganic products insoluble at pressures near the supercritical point of water (217 bar at 374 °C). Pressure was increased to the range 1 to 1.2 kbar to increase solubility, whereas previous reports were mostly in the range 250 to 400 bar. Removal of salts by filtration of pretreated mixtures, and use of mechanical solid collectors also help to avoid plugging. Carbon dioxide and other carriers are to be tested to determine whether advantages exist with non-aqueous systems, regarding flow rate, recycling, physical handling, and solubility of components. Acidic products tend to cause pitting or other corrosion of the inner surface of the reaction tube. This has been minimized or avoided by a pretreatment alkaline hydrolysis step, usually with sodium hydroxide, but also by ammonium hydroxide. Pretreatment is also used to increase reaction efficiency. Simultaneous addition of alkali has also been successful, if the insoluble solids formed can be handled to prevent plugging. Most common tube materials are stainless steels, Hastelloys, Inconels and other nickel or chromium based alloys. Inert liners or coatings in the reaction tube have also been effective to minimize corrosion from high pressures and low pH.

The oxidant was 10 to 30% aqueous hydrogen peroxide. The following DRE values resulted at 8 to 13 grams/minute throughput. The feed liquid contained up to 1 or 2% of the PEP or simulant by weight resulting in a processing rate of about 8 grams/hour treatment rate. The purpose of these runs was not high throughput, but proof that a high DRE could be attained. A larger supercritical reactor was set up to determine what throughput could be attained with a 1-inch schedule 80 seamless stainless steel tube reactor. A throughput of up to 31 gallons per hour was attained, equivalent to 260 pounds/hour, or 1 drum every two hours. One furnace can heat 10 lines, which would allow a throughput of five to six 55 gallon drums per hour.

NERVE AGENTS

Chemical nerve agents are typically organic phosphate esters. Tests conducted in this study used the commercially available insecticide Malathion as a simulant for nerve agents, because it also contains the toxic organic phosphate moiety. One of the structural names for Malathion is *S*-(1,2-dicarbethoxyethyl) *O,O*-dimethyldithiophosphate. The commercial sample was 57% in naphtha hydrocarbon carrier. The sulfur and phosphorus present in the Malathion structure gave acidic threat of corrosion (pH 1.3). But addition of sodium hydroxide to the reaction mixture raised the pH to 7 and increased the conversion. Salts were kept in solution by the higher reaction pressure 1.2 kbar. The high hydrocarbon content obscured the true conversion % of the Malathion itself, which was probably better than 99.99%, but 99.8% was proven by total organic carbon (TOC) mass balance. Previously published conversions at only 0.28 kbar showed >99.99999 %DRE for nerve agents⁶ GB and VX, >99.9999 for sulfur mustard⁶, >99.99% DRE

for dimethylmethylphosphonate⁷ (DMMP) a nerve agent simulant, and >99 %DRE for thiodiglycol,⁷ a mustard simulant. These examples provide confidence the higher pressure (1.2 kbar) attained in this study will give faster production with agents that are not mixed with hydrocarbon carriers.



RED-WATER

TNT Red water is a sulfite liquor from a purification step in the manufacture of 2,4,6-trinitoluene. The sulfite complexes of minor nitration products and other impurities in the TNT are removed in this liquor, which then becomes a waste stream for the TNT production line. Incineration has been used for treatment of this waste, with disadvantages such as high concentrations of acidic sulfur oxides in the flue gas. However, high-pressure hydrothermal oxidation allows conversion to sulfate type salts, which could be disposed of without much vapor problem, or neutralized and recovered as solid salts for recycle. In the supercritical conditions of this hydrothermal oxidation study, the salts are insoluble and can easily cause plugging. The pressure was increased to 1 kbar (1000 atmospheres, ~14.7k psi), which allowed sufficient solubility to avoid plugging at 430 °C. The highly acidic product (pH 1.8) should better be neutralized to avoid corrosion of the reactor, but efficacy of the method was proven with 99.9 %DRE based on conversion of organic carbon.

Composition of the red water is given by the following percentages from the ICI supplier:

32.3	Sodium sulfate and sulfite
11.2	Sodium nitrite
1.5	Sodium nitrate
22.7	Sodium sulfonate of 2,4,5-trinitrotoluene
16.2	Alpha-TNT-Sellite complex
9.6	Sodium sulfonate of 2,3,4-trinitrotoluene
2.0	Sodium sulfonate of 2,3,6-trinitrotoluene
1.0	Sodium salt of 2,4,6-trinitrobenzoic acid
1.0	Sodium salt of unknown structure
1.0	Bisulfite addition compound of trinitrobenzaldehyde
1.0	Trinitrobenzyl alcohol
0.5	Sodium nitroformate
traces	Sodium salts of nitroaromatic acids, carbonates, sulfides, 2,4-DNT, alpha-TNT

HYDROTHERMAL OXIDATION RESULTS

Items without inorganic constituents or products had high conversions at pressure just into the supercritical range (0.37 kbar). Increased pressure at about 1 kbar gave significantly improved solvation of inorganic salts. Higher ratio of surplus oxidant gave significantly faster reaction. Addition of alkali or pretreatment with alkali gave better reaction by hydrolysis while avoiding corrosion of the reactor. Good DRE was obtained at reasonable residence times at concentrations up to 1 or 2%. Conversions of 99.9 %DRE or better were obtained for nearly all items.

Table 3. Destruction and Removal Efficiency (DRE) for High-Pressure Hydrothermal Oxidation of Smoke Mixtures and PEP Related Items

	Total Organic Carbon DRE	Temp °C	Resid Press kbar	Equiv Time sec	Start Oxidant Ratio	End pH
Malathion/Naphtha/aq NaOH	99.8%	458	1.19	69	6.08	7.1/
Malathion/Naphtha/aq NaOH	99.8%	431	1.21	68	5.75	6.8/
Malathion/Naphtha	90.9%	478	1.10	68	2.19	1.3/
Malathion/Naphtha	74.1%	421	1.09	82	2.26	1.5/
TNT Red Water	99.9%	448	1.04	85	2.84	1.8/
TNT Red Water	99.8%	429	1.05	90	2.26	1.8/
Yellow Smoke Mix	99.9%	442	1.04	94	3.60	6.4/
Yellow Smoke Mix	>99.9%	468	1.01	72	2.89	
Violet Smoke Mix	>99.9%	452	1.14	70	2.55	2.9/
Violet Smoke Mix	99.8%	442	1.08	71	2.99	4.6/
Green Smoke Mix	>99.9%	442	1.15	64	2.30	6.8/
Green Smoke Mix	>99.9%	458	1.14	56	2.02	6.3/
Green Smoke Mix	>99.9%	472	1.15	54	1.99	6.4/
Red Smoke Mix	99.9%	468	1.15	66	2.59	5.8/
Red Smoke Mix	98.8%	443	1.16	69	2.58	6.1/
2,6-Dinitrotoluene	>99.99%	490	0.405	32	1.25	
3,4-Dinitrotoluene	>99.99%	493	0.369	27	1.12	
2,4,6-Trinitrotoluene	>99.99%	487	0.372	28	1.43	
Comp-B3/aq NaOH, filtered	>99.99%	444	1.11	61	1.20	11/7.3
Comp-B3/aq NaOH, filtered	99.75%	442	0.71	89	0.93	11/7.9
Comp-B3/aq NaOH, filtered	99.52%	427	0.71	98	0.96	11/7.8
Comp-B3/aq NaOH, filtered	99.49%	412	0.70	105	0.99	11/7.8
Comp-B3/aq NaOH, filtered	99.11%	392	0.69	108	0.95	11/7.7
Comp-B3/aq NaOH, filtered	97.50%	374	0.34	95	1.18	11/7.6
PBX-9404/aq NaOH, filtered	>99.99%	437	1.09	61	0.74	13/7.7
PBX-9404/aq NaOH, filtered	>99.99%	455	1.10	57	1.08	13/7.6
PBX-9404/aq NaOH, filtered	>99.99%	455	1.11	62	0.85	13/7.5
PBX-9404/aq NaOH, filtered	>99.99%	411	1.12	64	0.83	13/7.5
PBX-9404/aq NaOH, filtered	99.50%	469	1.12	53	0.50	13/8.6
PBX-9404/aq NaOH, filtered	99.26%	375	0.33	54	0.94	13/7.6
PBX-9404/aq NaOH, filtered	86.06%	377	0.32	285	0.05	13/9.4

REFERENCES

1. Demilitarization of Bulk Smoke Mixes and Smoke Signals, Larry Higley, Ammunition Equipment Directorate, Tooele Army Depot, Utah 84074, April 1995.
2. Hydrothermal Oxidation: A Technology for Energetic Materials and Chemical Warfare Agents, Philip Dell'Orco, Edwin Eaton and Raymond Flesner, LA-UR-95-3615, HE Science and Technology (DX-2), Los Alamos National Laboratory, New Mexico 87545, Dec 1995.
3. RCRA Upgrade of APE-1236 Deactivation Furnaces, J. L. Bishop, R. G. Anderson and M. M. Zaugg, Ammunition Equipment Directorate, Tooele Army Depot, Utah 84074-5004, presented at the International Seminar on Demilitarization Technology for Explosives and Explosive Ordnance, 21 & 22 Nov 1991, Royal Military College of Science, Shrivenham, Swindon, Wiltshire, England.
4. a) APE-1236M1 Operation and Maintenance Manual, Ammunition Equipment Directorate, Tooele Army Depot, Utah 84074, Apr 1996; b) Explosive Waste Incinerator Operation Manual T377, p 3-30, Feb 1982.
5. APE-1236 Trial Burn Test Reports written by the Army Environmental Hygiene Agency, now Army Center for Health Promotion and Preventative Medicine, for following installations: a) Mississippi Army Ammunition Plant, Picayune, Mississippi 39466, Dec 1985; b) Lake City Army Ammunition Plant, Independence, Missouri 64051, Oct 1992; c) Kansas Army Ammunition Plant, Parsons, Kansas 67357, Jul 1995; d) Iowa Army Ammunition Plant, Middletown, Iowa 52638, Jul 1993; e) Tooele Army Depot, Utah 84074, Dec 1993.
6. Hydrothermal Oxidation as an Environmentally Benign Treatment Technology, General Atomics, Inc., JANNAF conference, San Diego CA, Jul 12, 1995.
7. Supercritical Water Oxidation of Dimethylmethyl Phosphonate and Thiodiglycol, M. Turner, PhD Thesis, University of Texas at Austin, Fall, 1993.